

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

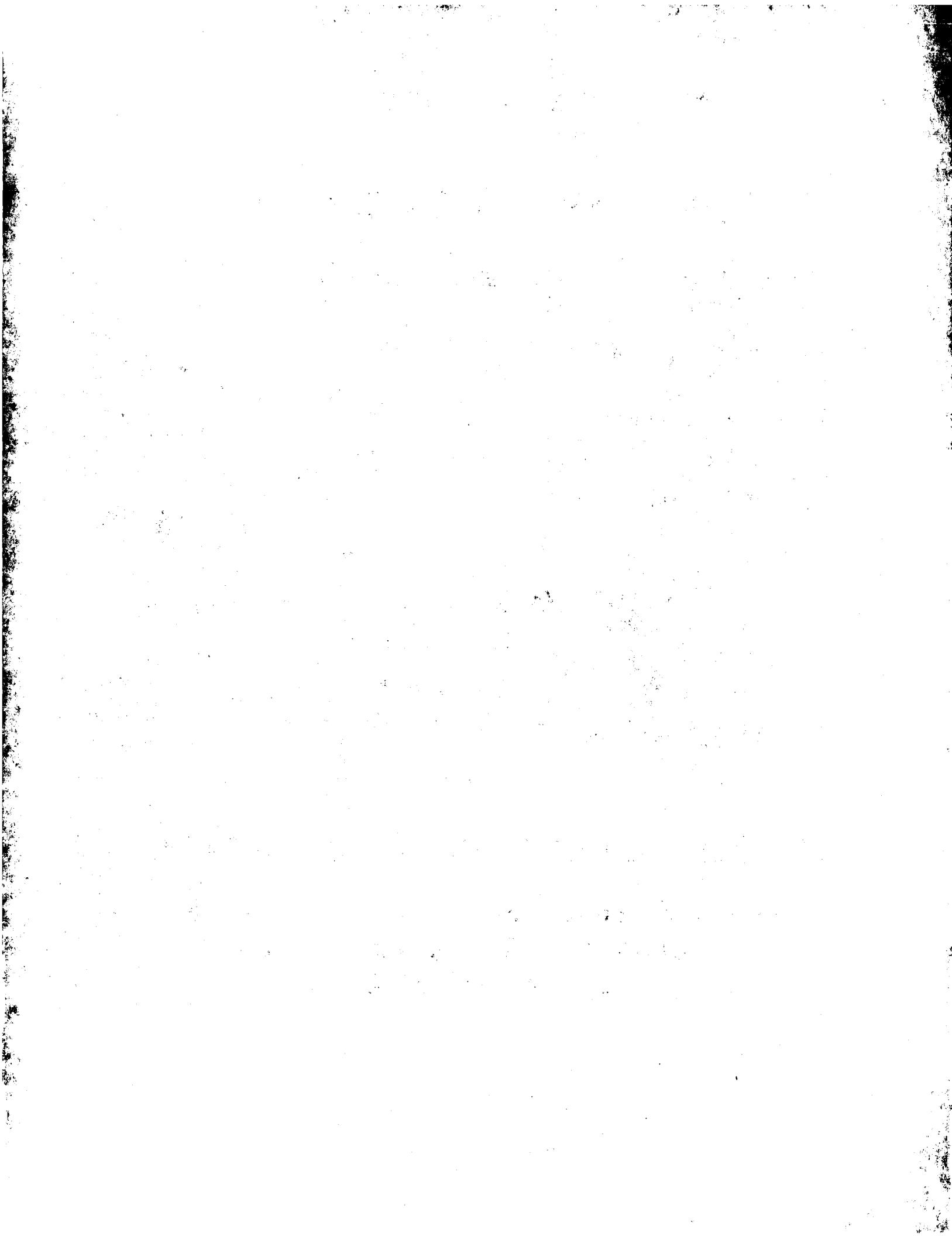
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problems Mailbox.**



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



A

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :	B01J 31/00, 31/26, 31/38	A1	(11) International Publication Number:	WO 96/14154
			(43) International Publication Date:	17 May 1996 (17.05.96)
(21) International Application Number:	PCT/US95/11976		(81) Designated States:	AU, CA, CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date:	20 September 1995 (20.09.95)			
(30) Priority Data:	333,684	3 November 1994 (03.11.94)	US	Published <i>With international search report.</i>
(71) Applicant:	MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).			
(72) Inventors:	MINK, Robert; Ivan; 30 A Gates Avenue, Warren, NJ 07059-5732 (US). NOWLIN, Thomas, Edward; 7 Perrine Path, Cranbury, NJ 08512 (US). SHIRODKAR, Pradeep, Pandurang; 8 McIntire Drive, Belle Mead, NJ 08502 (US). SCHREGENBERGER, Sandra, Denise; 5 Hope Court, Neshanic, NJ 08853 (US). TSIEN, Grace, Onkee; 78 Elm Street, Colonia, NJ 07067 (US).			
(74) Agents:	SCHNELLER, Marina, V. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).			

(54) Title: CATALYST FOR BIOMODAL MOLECULAR WEIGHT DISTRIBUTION ETHYLENE POLYMERS AND COPOLYMERS

(57) Abstract

The interaction of silica, previously calcined at 600 °C, with dibutylmagnesium (DBM), 1-butanol and titanium tetrachloride and a solution of methylalumoxane (MAO) and $(BuCp)_2ZrCl_2$ provides a catalyst that, in the absence of a trialkylaluminum (AlR_3) cocatalyst, produces polyethylene with a bimodal MWD.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

-1-

CATALYST FOR BIMODAL MOLECULAR WEIGHT DISTRIBUTION
ETHYLENE POLYMERS AND COPOLYMERS

The invention relates to a catalyst and its use in the preparation of bimodal molecular weight distribution (MWD) polymers and copolymers of ethylene, in one reactor. The catalyst comprises at least two transition metal components 5 on a support; one of the two transition metal components is provided in the form of a metallocene. The supported transition metals are activated by oligomeric and/or polymeric oxygen-containing compounds of aluminum.

Products of polymerization in the presence of the catalysts 10 comprise two components with significantly different molecular weights, thus one being of relatively higher molecular weight than the other; such polymerization products are referred to as bimodal molecular weight distribution products.

15 The catalysts can be run in a conventional gas phase fluidized bed reactor without reactor fouling and without using an alumoxane cofeed to the polymerization reactor. Accordingly, the catalyst of the invention is useful in continuous polymerization and copolymerization of ethylene 20 in a single conventional gas phase fluidized bed reactor without reactor fouling.

Figure 1 is a gel permeation chromatogram of a bimodal molecular weight distribution product of the Examples. These polymerization products comprise two 25 components of different molecular weights, thus one being of relatively higher molecular weight than the other.

The catalysts will be discussed in terms of their method of preparation below:

A supported non-metallocene transition metal compound, 30 free of an activator such as an alkylaluminum (e.g., trialkylaluminum, dialkylaluminum halides and hydrides), referred hereinafter as non-metallocene transition metal, is activated by contacting with a solution containing an alumoxane alone or in admixture with a metallocene

compound. The invention relates to a catalyst and its use in the preparation of bimodal molecular weight distribution polymers and copolymers of ethylene, prepared in one reactor. The catalyst comprises at least two transition metal components on a support; one of the two transition metal components is provided in the form of a metallocene. The supported transition metals are activated during catalyst preparation. In accordance with the invention, no aluminum alkyl compound feed to the reactor (slurry or gas phase fluidized bed) is required.

In a preferred embodiment, the catalysts of the invention consist of a supported non-metallocene transition metal component, a metallocene transition metal compound and methylalumoxane.

The carrier material is a solid, particulate, porous, preferably inorganic material, such as an oxide of silicon and/or of aluminum. The carrier material is used in the form of a dry powder having an average particle size of from 1 micron to 500 microns, preferably from 10 microns to 250 microns. The surface area of the carrier is at least 3 square meters per gram (m^2/g), and preferably at least 50 m^2/g up to 350 m^2/g . The carrier material should be dry, that is, free of absorbed water. Drying of the carrier material can be effected by heating at 100°C to 1000°C, preferably at 600°C. When the carrier is silica, it is heated to at least 200°C, preferably 200°C to 850°C and most preferably at 600°C. The carrier material must have at least some active hydroxyl (OH) groups to produce the catalyst composition of this invention.

In the most preferred embodiment, the carrier is silica which, prior to the use thereof in the first catalyst synthesis step, has been dehydrated by fluidizing it with nitrogen and heating at 600°C for 16 hours to achieve a surface hydroxyl group concentration of 0.7 millimoles per gram (mmol/g). The silica of the most preferred embodiment is a high surface area, amorphous

-3-

silica (surface area = 300 m²/g; pore volume of 1.65 cm³/g), and it is a material marketed under the tradenames of Davison 952 or Davison 955 by the Davison Chemical Division of W.R. Grace and Company. The silica is in the form of spherical particles, e.g., as obtained by a spray-drying process. As procured, these silicas are not calcined; and this must be dehydrated, as indicated above.

The catalyst synthesis is undertaken under inert conditions, in the absence of water and of oxygen.

The carrier material, having said (OH) groups, is slurried in a non-polar solvent and the resulting slurry is contacted with at least one organomagnesium compound having the empirical formula below. The slurry of the carrier material in the solvent is prepared by introducing the carrier into the solvent, preferably while stirring, and heating the mixture to 25 to 70°C, preferably to 40 to 60°C. Temperatures here are critical with respect to the non-metallocene transition metal which is subsequently added; that is temperatures in this slurry of 90°C or higher result in deactivation of the non-metallocene transition metal added subsequently. Accordingly, all catalyst precursor synthesis steps are conducted below 90°C. The slurry is then contacted with the aforementioned organomagnesium compound, while the heating is continued as indicated.

The organomagnesium compound has the empirical formula RMgR'

where R and R' are the same or different C₂-C₁₂ alkyl groups, preferably C₄-C₁₀ alkyl groups, more preferably C₄-C₆ alkyl groups, and most preferably both R and R' are mostly butyl groups.

Suitable non-polar solvents are materials in which the reactants used herein, i.e., the organomagnesium compound, and the non-metallocene transition metal compound, are soluble. Preferred non-polar solvents are alkanes, such as isopentane, hexane, n-heptane, octane, nonane, and decane,

although a variety of other materials including cycloalkanes, such as cyclohexane, aromatics, such as benzene, toluene and ethylbenzene, may also be employed. The most preferred non-polar solvent is isopentane. Prior to use, the non-polar solvent should be purified, such as by percolation through silica gel and/or molecular sieves, to remove traces of water, oxygen, polar compounds, and other materials capable of adversely affecting catalyst activity.

In the most preferred embodiment of the synthesis of this catalyst it is important to add only such an amount of the organomagnesium compound that will be deposited - physically or chemically - onto the support since any excess of the organomagnesium compound in the solution may react with other synthesis chemicals and precipitate outside of the support. The carrier drying temperature affects the number of sites on the carrier available for the organomagnesium compound - the higher the drying temperature the lower the number of sites. Thus, the exact molar ratio of the organomagnesium compound to the hydroxyl groups will vary and must be determined on a case-by-case basis to assure that only so much of the organomagnesium compound is added to the solution as will be deposited onto the support without leaving any excess of the organomagnesium compound in the solution. Thus, the molar ratios given below are intended only as an approximate guideline and the exact amount of the organomagnesium compound in this embodiment must be controlled by the functional limitation discussed above, i.e., it must not be greater than that which can be deposited onto the support. If greater than that amount is added to the solvent, the excess may react with the non-metallocene transition metal compound, thereby forming a precipitate outside of the support which is detrimental in the synthesis of our catalyst and must be avoided. The amount of the organomagnesium compound which is not greater than that

-5-

deposited onto the support can be determined in any conventional manner, e.g., by adding the organomagnesium compound to the slurry of the carrier in the solvent, while stirring the slurry, until the organomagnesium compound is

5 detected in the solvent.

For example, for the silica carrier heated at 600°C, the amount of the organomagnesium compound added to the slurry is such that the molar ratio of Mg to the hydroxyl groups (OH) on the solid carrier is 0.5:1 to 4:1, preferably 0.8:1 to 3:1, more preferably 0.9:1 to 2:1 and most preferably 1:1. The organomagnesium compound dissolves in the non-polar solvent to form a solution from which the organomagnesium compound is deposited onto the carrier.

10 It is also possible to add such an amount of the organomagnesium compound which is in excess of that which will be deposited onto the support, and then remove, e.g., by filtration and washing, any excess of the organomagnesium compound. However, this alternative is

15 less desirable than the most preferred embodiment described above.

20 The organomagnesium treated support is contacted with an organic alcohol reagent ($R''OH$). The amount of this organic alcohol reagent is effective to provide a $R''OH:Mg$ ratio of 0.5 to 2.0, preferably 0.8 to 1.5.

25 Contact of the silica supported magnesium compound, with the organic alcohol reagent is undertaken in the slurry. Contact is undertaken at a temperature ranging from 25°C to 90°C, preferably 40°C to 60°C.

30 The alkyl group in the organic alcohol reagent can contain 1 to 12 carbon atoms, preferably 1 to 8; in the embodiments below, it is an alkyl containing 2 to 4 carbon atoms, particularly of 4 carbon atoms (butyl). The inclusion of the alcohol reagent step in the catalyst

35 synthesis of the invention produces a catalyst which, relative to the absence of this step, is much more active,

requires much less non-metallocene transition metal compound (e.g. titanium), and is much more active with respect to the product component produced with the metallocene component.

5 After the addition of the organic alcohol reagent to the slurry is completed, the slurry is contacted with a non-metallocene transition metal compound. The slurry temperature must be maintained at 25 to 90°C, preferably to 10 40 to 60°C. As noted above, temperatures in this slurry of 90°C or greater result in deactivation of the catalyst. Suitable non-metallocene transition metal compounds used herein are compounds of metals of Groups 4, and 5, of the Periodic Chart of the Elements, as published by Chemical and Engineering News, 63(5), 27, 1985, providing that such 15 compounds are soluble in the non-polar solvents. Non-limiting examples of such compounds are titanium and vanadium halides, e.g., titanium tetrachloride, $TiCl_4$, vanadium tetrachloride, VCl_4 , vanadium oxytrichloride, $VOCl_3$, titanium and vanadium alkoxides, wherein the 20 alkoxide moiety has a branched or unbranched alkyl radical of 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms. The preferred transition metal compounds are titanium compounds, preferably tetravalent titanium compounds. The most preferred titanium compound is titanium tetrachloride. 25 The amount of titanium or vanadium, in non-metallocene form ranges from a Ti/Mg molar ratio of 0.3 to 1.0, preferably from 0.50 to 0.80.

Mixtures of such non-metallocene transition metal compounds may also be used and generally no restrictions 30 are imposed on the transition metal compounds which may be included. Any transition metal compound that may be used alone may also be used in conjunction with other transition metal compounds.

After the addition of the non-metallocene transition 35 metal compound is complete, the slurry solvent is removed by evaporation or filtering to obtain a free-flowing

-7-

powder. Next, incorporation of the metallocene component can be undertaken. The metallocene is activated with an alumoxane. The metallocene compound has the formula $Cp_xMA_yB_z$, in which Cp is an unsubstituted or substituted cyclopentadienyl group, M is zirconium or hafnium and A and B belong to the group including a halogen atom, hydrogen atom or an alkyl group. In the above formula of the metallocene compound, the preferred transition metal atom M is zirconium. In the above formula of the metallocene compound, the Cp group is an unsubstituted, a mono- or a - polysubstituted cyclopentadienyl group: and x is at least 1. The substituents on the cyclopentadienyl group can be preferably straight-chain C₁-C₆ alkyl groups. The cyclopentadienyl group can be also a part of a bicyclic or a tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. In the case when x in the above formula of the metallocene compound is equal to 2, the cyclopentadienyl groups can be also bridged by polymethylene or dialkylsilane groups, such as -CH₂-, -CH₂-CH₂-, -CR'R"- and -CR'R"-CR'R"- where R' and R" are short alkyl groups or hydrogen atoms, -Si(CH₃)₂-, Si(CH₃)₂-CH₂-CH₂-Si(CH₃)₂- and similar bridge groups. The A and B substituents in the above formula of the metallocene compound may be halogen atoms; and y + z is 3 or less, provided that x + y + z equals the valence of M. If the substituents A and B in the above formula of the metallocene compound are alkyl groups, they are preferably straight-chain or branched C₁-C₆ alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl or n-octyl.

Suitable metallocene compounds include
bis(cyclopentadienyl)metal dihalides,
bis(cyclopentadienyl)metal hydridohalides,
35 bis(cyclopentadienyl)metal monoalkyl monohalides,
bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal

-8-

dihalides wherein the metal is zirconium or hafnium, halide groups are preferably chlorine and the alkyl groups are C₁-C₆ alkyls. Illustrative, but non-limiting examples of metallocenes include bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)zirconium hydridochloride, 1,2-ethylene bis(indenyl)zirconium dichloride, 1,1-ethylene bis(indenyl)zirconium dichloride, bis(cyclopentadienyl)hafnium hydridochloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dimethyl, bis(n-butylcyclopentadienyl)hafnium dimethyl, bis(n-butylcyclopentadienyl)zirconium hydridochloride, bis(n-butylcyclopentadienyl)hafnium hydridochloride, bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, cyclopentadienyl-zirconium trichloride, bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)] zirconium dichloride. The metallocene compounds utilized within the embodiment of this art can be used as crystalline solids, as solutions in hydrocarbons or in a supported form.

The alumoxane can be impregnated into the carrier at any stage of the process of catalyst preparation. In this embodiment, the amount of Al, provided by alumoxane, is sufficient to provide an Al:transition metal (provided by metallocene) molar ratio ranging from 50 to 500, preferably 75 to 300.

The class of alumoxanes comprises oligomeric linear and/or cyclic alkylalumoxanes represented by the formula:

-9-

R-(Al(R)-O)_n-AlR₂ for oligomeric, linear alumoxanes and (-Al(R)-O-)_m for oligomeric cyclic alumoxanes wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C₁-C₈ alkyl group and preferably methyl.

5 MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of 1200. Methylalumoxane is commonly produced by reacting trimethylaluminum with water or with hydrated inorganic salts, such as CuSO₄.5H₂O or Al₂(SO₄)₃.5H₂O.

10 Methylalumoxane can be also generated in situ in polymerization reactors by adding to the reactor trimethylaluminum and water or water-containing inorganic salts. MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an

15 average molecular weight of 1200. MAO is typically kept in solution in toluene. Both the titanium and zirconium active sites may be activated by commercially-available methylalumoxane. The most preferred activator for the zirconium sites is methylalumoxane. In the most preferred

20 embodiment the addition of such a commercial methylalumoxane to the catalyst precursor is sufficient to activate both the zirconium sites and the titanium and/or vanadium sites.

Incorporation of the activated metallocene component onto the carrier can be accomplished in various ways. Incorporation of either or both the alumoxane and the metallocene compound can be into the slurry resulting from the addition, i.e. after the addition, of the non-metallocene transition metal compound.

30 Alternatively, and in accordance with the unique method of infusion of alumoxane into the pores of the carrier, the carrier slurry can be stripped of solvent, after the addition of the non-metallocene transition metal compound, to form a free-flowing powder. The free flowing

35 powder can then be impregnated by determining the pore volume of the carrier and providing an alumoxane (or

-10-

metallocene-alumoxane) solution in a volume equal to or less than the total pore volume of the carrier, and recovering a dry catalyst precursor. The resulting free-flowing powder does not need to be combined with an activator (sometimes referred as a cocatalyst) in the polymerization reactor.

The volume of the solution comprising the alumoxane and a solvent therefor can vary. In a preferred embodiment, of alumoxane incorporation into the carrier, one of the controlling factors in the alumoxane incorporation into the carrier material catalyst synthesis is the pore volume of the support. In this preferred embodiment, the process of impregnating the carrier material is by infusion of the alumoxane solution, without forming a slurry of the carrier material, such as silica, in the alumoxane solution. The volume of the solution of the alumoxane is sufficient to fill the pores of the carrier material without forming a slurry in which the volume of the solution exceeds the pore volume of the silica; accordingly and preferably, the maximum volume of the alumoxane solution is, does not exceed, the total pore volume of the carrier material sample. That maximum volume of the alumoxane solution insures that no slurry of the carrier material is formed. Accordingly, if the pore volume of the carrier material is $1.65\text{cm}^3/\text{g}$, then the volume of alumoxane solution will be equal to or less than $1.65\text{ cm}^3/\text{g}$ of carrier material. As a result of this proviso, the impregnated carrier material will appear dry immediately following impregnation although the pores of the carrier will be filled with inter alia solvent.

Solvent may be removed from the alumoxane impregnated pores of the carrier material by heating and/or under a positive pressure induced by a flow of an inert gas, such as nitrogen. If employed, the conditions in this step are controlled to reduce, if not to eliminate, agglomeration of impregnated carrier particles and/or crosslinking of the

-11-

alumoxane. In this step, solvent can be removed by evaporation effected at relatively low elevated temperatures of above 40°C and below 50°C to obviate agglomeration of catalyst particles and crosslinking of the alumoxane. Although solvent can be removed by evaporation at relatively higher temperatures than that defined by the range above 40°C and below 50°C, very short heating times schedules must be employed to obviate agglomeration of catalyst particles and crosslinking of the alumoxane or catalyst deactivation.

In a preferred embodiment, the metallocene is added to the solution of the alumoxane prior to impregnating the carrier with the solution. Again, as noted above, the maximum volume of the alumoxane solution also including the metallocene is the total pore volume of the carrier material sample. The molar ratio of alumoxane provided aluminum, expressed as Al, to metallocene metal expressed as M (e.g. Zr), ranges from 50 to 500, preferably 75 to 300, and most preferably 100 to 200. An added advantage of the present invention is that this Al:Zr ratio can be directly controlled. In a preferred embodiment the alumoxane and metallocene compound are mixed together at a temperature of 20 to 80°C, for 0.01 to 6.0 hours, prior to use in the infusion step. The solvent for the metallocene and alumoxane can be appropriate solvents, such as aromatic hydrocarbons, ethers, cyclic ethers or esters, preferably it is toluene.

The catalyst precursor component formed from the organomagnesium compound, the non-metallocene transition metal compound and the activated metallocene, need not be further activated with a cocatalyst, such as an alkylaluminum compound. Moreover, use of this catalyst does not require alumoxane cofeed to the reactor.

The amount of alumoxane is sufficient to give an Al:Ti molar ratio of 5:1 to 1000:1, preferably 15:1 to 300:1, and most preferably 20:1 to 100:1. The catalyst exhibits high

activity for long periods of time, and exhibits little deactivation.

The catalyst can be fed to the fluidized bed reactor for gas phase polymerizations and copolymerizations of ethylene in particulate form. Moreover, in accordance with the invention, the catalyst can be fed to the fluidized bed reactor for polymerizations and copolymerizations of ethylene in the absence of alumoxane solution. It is essential to operate the fluidized bed reactor at a temperature below the sintering temperature of the polymer particles. For the production of ethylene copolymers in the process of the present invention an operating temperature of 30° to 115°C is preferred, and a temperature of 75° to 95°C is most preferred. Temperatures of 75° to 10 90°C are used to prepare products having a density (g/cc) of 0.91 to 0.92, and temperatures of 80° to 100°C are used to prepare products having a density of 0.92 to 0.94, and temperatures of 90° to 115°C are used to prepare products having a density of 0.94 to 0.96. A fluidized bed reactor 15 polymerization in accordance is operated at pressures of up to 1000 psi, and is preferably operated at a pressure of from 150 to 350 psi, with operation at the higher pressures in such ranges favoring heat transfer since an increase in pressure increases the unit volume heat capacity of the 20 gas.

Products

In accordance with the invention, polyethylene with a bimodal MWD can be prepared in a single reactor by the catalyst of this invention without adding a separate 30 aluminumalkyl cocatalyst to the polymerization reactor. Specifically, a supported non-metallocene transition metal compound, free of an activator therefor such as an alkylaluminum compound (e.g., trialkylaluminum, dialkylaluminum halides and hydrides), is activated by 35 contacting the supported catalyst containing a non-

-13-

metallocene transition metal with a solution containing both a metallocene compound and an aluminoxane compound. No separate feed of alumoxane or a trialkyl aluminum compound to the polymerization reactor (slurry or fluidized bed) is necessary. In titanium/zirconocene-based bimetallic catalyst systems the LMW component is produced by the Zr site, while the HMW component is produced by the Ti site. The relative productivity of the two sites determines the weight fraction of each of the HMW/LMW components in the final product. As with typical Ziegler/Natta catalysts, an aluminumalkyl cocatalyst is usually added to the polymerization reactor (either slurry or gas phase) in order to activate the catalyst to produce polyethylene.

Polymerization products comprise two components of different molecular weight, with one MW component being of relatively higher molecular weight than the other. The relatively higher molecular weight component, of the bimodal molecular weight distribution product, has a relatively narrow molecular weight distribution.

Ethylene polymers, as well as copolymers of ethylene with one or more C₃-C₁₀ alpha-olefins, can be produced in accordance with the invention. Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/1-butene copolymers, ethylene/1-hexene copolymers and ethylene/4-methyl-1-pentene copolymers.

Hydrogen may be used as a chain transfer agent in the polymerization reaction of the present invention. The ratio of hydrogen/ethylene employed will vary between 0 to 2.0 moles of hydrogen per mole of ethylene in the gas phase. Any gas inert to the catalyst and reactants can also be present in the gas stream.

Ethylene/1-butene and ethylene/1-hexene copolymers are the most preferred copolymers polymerized in the process of

-14-

and with the catalyst of this invention. The ethylene copolymers produced in accordance with the present invention preferably contain at least 70 percent by weight of ethylene units. The catalyst of this invention can also be used to polymerize propylene and other alpha-olefins and to copolymerize them.

In another embodiment of the invention, the catalyst of the invention exhibits high activity for polymerization of ethylene and higher alpha-olefins and allows the synthesis of ethylene polymers and copolymers with a broad molecular weight distribution and generally, bimodal molecular weight distribution with a relatively high molecular weight component and with a relatively lower molecular weight component in the resin blend. The molecular weight distribution of the bimodal resin, expressed as Melt Flow Ratio, is 70 to 200.

(EXAMPLE 1)

CATALYST PREPARATION

The titanium component of the catalyst was prepared as described in Example 1A. The zirconium component of the catalyst was prepared using a physical "dry" impregnation method described in U. S. Patent No. 5,332,706, which is relied upon and incorporated by reference herein.

(EXAMPLE 1A)

TITANIUM CATALYST PREPARATION: .955 silica calcined at 600°C (541g) was weighted into a two-gallon stainless steel autoclave containing a stirring paddle. Next, ca. 4.8 liters of dry isopentane was added to the autoclave and the stirring rate was set at 100 rpm. The temperature of the silica/isopentane slurry was 54-58°C. Next, dibutylmagnesium (389 mmol) was added to the slurry. The contents of the autoclave were stirred for 60 minutes. Then 1-butanol (468 mmol) was added and stirring was

-15-

continued for one hour. Finally, titanium tetrachloride (233 mmol) was added to the autoclave and stirring continued for 60 minutes. After this time, all solvents were removed by evaporation under a nitrogen purge. The
5 yield of the non-metallocene transition metal component was 480 grams of a white-free flowing powder. Ti found 1.60 wt%; Mg found 1.38 wt%.

(EXAMPLE 1B)

FINISHED BIMETALLIC CATALYST PREPARATION: Solution (A):
10 (BuCp)₂ZrCl₂ (0.096 g, 0.237 mmol) was transferred to a 30 ml serum-bottle and 5.0 ml (4.68 g) of a 4.75 Molar Al (14.1 wt% Al) solution of methylalumoxane were added. The bottle was shaken for one minute to form a solution which was used immediately as described below.
15 Under an inert atmosphere, 2.5 grams of the titanium-containing component described in EXAMPLE 1A was added to a 200 ml pear-flask containing a magnetic stirring bar which was used to agitate the catalyst powder vigorously. Then at room temperature, 3.7 ml of solution (A) described above, was added dropwise to the flask over a 10 minute period. The total volume of solution (A) used was such that the titanium containing catalyst always appeared dry during the entire addition time. However, during this addition time, the white titanium-containing catalyst
20 turned a dark brown color. Finally, the pear flask was placed into an oil bath set at 55-60°C, and the residual toluene from solution (A) was removed with a nitrogen purge to give a dry, tan, free-flowing powder. Ti: 1.09 wt%; Mg 0.91 wt%; Al 13.1 wt%; Zr 0.42 wt%.

30 (EXAMPLE 2)

POLYMERIZATION - Slurry

Polymerization: Ethylene/1-hexene copolymer was prepared with the bimetallic (Ti/Zr) catalyst of EXAMPLE 1B

-16-

above to produce HDPE with a relatively high molecular weight.

A 1.6 liter stainless steel autoclave, at 47°C, was filled with 0.750 liters of dry hexane, 0.030 liters of dry 5 1-hexene while under a slow nitrogen purge. NOTE: No aluminumalkyl cocatalyst was added to the reactor. Next, the reactor vent was closed, the stirring rate was set at 900 rpm, the internal temperature was increased to 85°C, and the internal pressure was raised from 5 psi to 13 psi 10 with hydrogen. Ethylene was introduced to maintain the reactor pressure at 200 psi. Next, 0.103 grams of catalyst described in Example 1B was introduced into the reactor with ethylene over-pressure and the temperature was increased and held at 95°C. The polymerization was 15 continued for 60 minutes, and then the ethylene supply was stopped and the reactor allowed to cool to room temperature. 70.8 grams of polyethylene were collected. The HLDI of the polymer was 2.3 indicating a relatively high molecular weight and the GPC chromatogram of this 20 polymer is shown in Figure 1.

DISCUSSION:

The molecular weight distribution (MWD) of polymer from the slurry reactor was examined by Gel Permeation Chromatography (GPC), and the result clearly shows that the 25 polymer has a bimodal MWD with a relatively HMW and relatively LMW component.

-17-

CLAIMS:

1. An activated catalyst composition for producing bimodal molecular weight distribution high density and linear low density polymers and copolymers of ethylene,
5 comprising

a dry, anhydrous, support containing composition comprising at least two transition metals one of which is provided as a metallocene compound and a second of which is provided as a transition metal source selected from the
10 group consisting of non-metallocene compounds,

wherein the catalyst is formed by depositing the transition metal source on the support, and contacting the supported non-metallocene transition metal source with a solution containing at least one source of aluminum and selected from the group consisting of alumoxane alone and
15 aluminoxane admixed with metallocene transition-metal compound in amounts effective to activate the two transition metals.

2. The catalyst of Claim 1 wherein the support is the reaction product of (1) silica having OH groups, impregnated with RMgR', wherein each of R and R' is an alkyl group of 4 to 10 carbon atoms,

5 wherein RMgR' is present in an amount to provide a RMgR':OH molar ratio of 0.5:1 to 3:1;

and (2) an organic alcohol reagent providing alkoxy groups having a formula R"O-, wherein R" is an alkyl group of 1 to 12 carbons;

10 wherein said reagent is used in an amount effective to provide an alcohol/Mg molar ratio of 0.5 to 2.0.

3. The catalyst of Claim 1 wherein the activated metallocene compound of a transition metal is a zirconocene.

4. The catalyst of Claim 2, wherein each of R and R' is an alkyl group of 4 to 8 carbon atoms.

-18-

5. The catalyst of Claim 2, wherein each of R and R' is a butyl group.

6. The catalyst of Claim 2, wherein R is an alkyl group of 1 to 12 carbons.

7. The catalyst of Claim 2, wherein R''O- is provided as an alcohol.

8. The catalyst of Claim 2, wherein the reaction product is formed by

(i) providing a slurry of a non-polar solvent and a solid porous silica having -OH groups;

5 (ii) impregnating said silica, with RMgR', to form an intermediate (ii), wherein the Mg:OH molar ratio is less than 2, wherein each of said R and R' is an alkyl group of 4 to 10 carbon atoms and is the same or different, wherein said RMgR' is soluble in said non-polar solvent;

10 (iii) treating the intermediate (ii) with an amount of R''OH, which amount is effective to provide a R''OH:RMgR' molar ratio of 0.5 to 2.0 to form a step (iii) product.

9. The catalyst of Claim 8, wherein the non-metallocene transition metal is titanium.

10. The catalyst of Claim 9, wherein the non-metallocene transition metal is titanium tetrachloride.

11. The catalyst of Claim 10, which further includes a step (iv), after (iii), comprising

treating the step (iii) product with TiCl₄, to form a titanium containing intermediate; and

5 (v) combining the titanium containing intermediate with a methylalumoxane solution containing a metallocene transition metal compound.

12. The catalyst of Claim 11 wherein the activator is methylalumoxane.

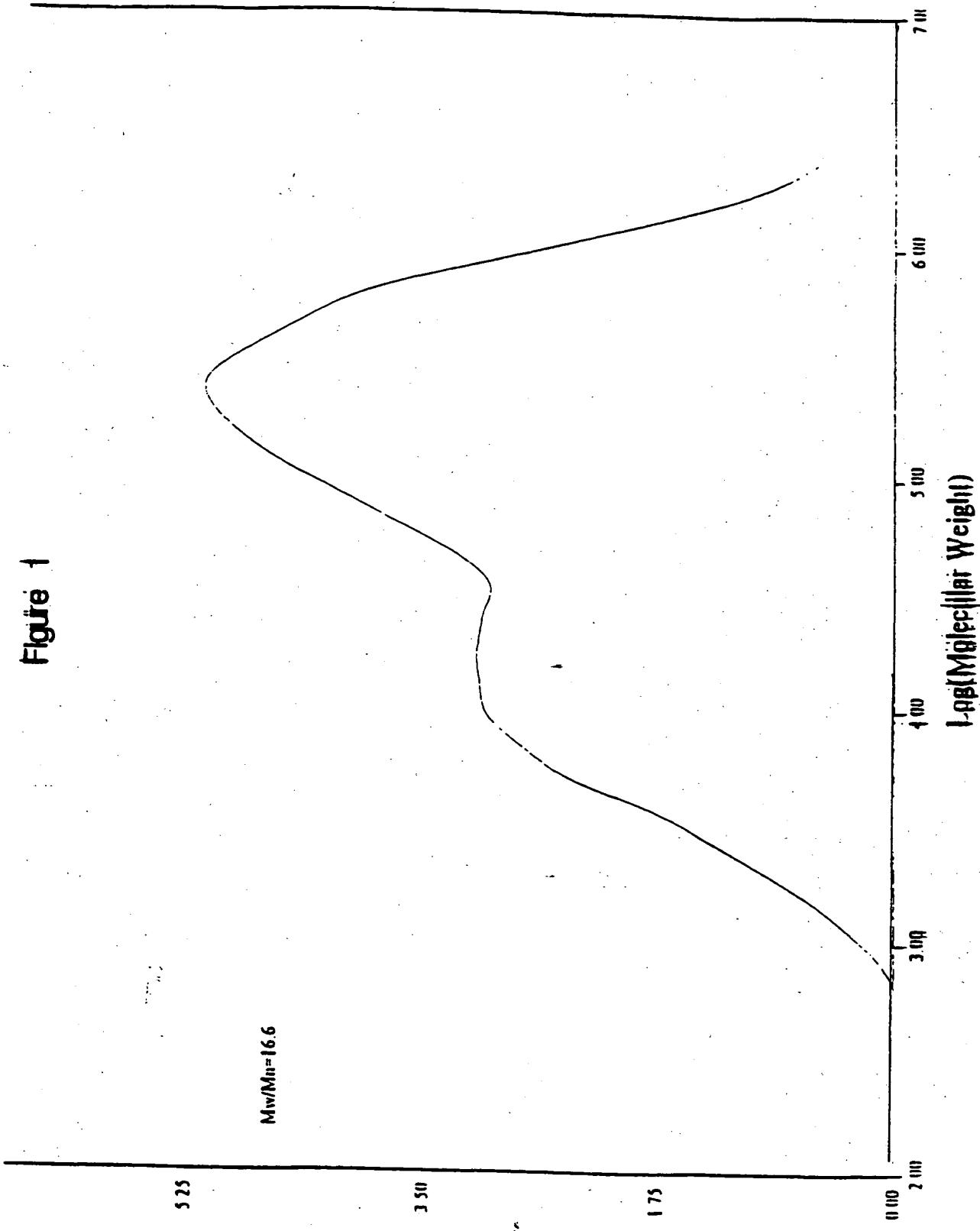
-19-

13. The catalyst of Claim 1, wherein the metallocene transition metal is provided as a compound which has the formula $Cp_xMA_yB_z$, wherein Cp is a cyclopentadienyl group or a cyclopentadienyl group which is part of a bicyclic or a tricyclic moiety such as indenyl, unsubstituted or substituted by an alkyl or alkylene group of 1 to 6 carbon atoms; x is at least 1; each of A and B is a halogen atom or an alkyl group of 1 to 8 carbon atoms, and y plus z is 3 or less provided that x+y+z is equal to the valence of M, which is selected from the group consisting of titanium or zirconium or hafnium.

14. The catalyst of Claim 11, wherein the metallocene transition metal is provided as a compound which has the formula $Cp_xMA_yB_z$, wherein Cp is a cyclopentadienyl group unsubstituted or substituted by an alkyl or alkylene group of 1 to 6 carbon atoms; x is at least 1; each of A and B is a halogen atom or an alkyl group of 1 to 8 carbon atoms, and y plus z is 3 or less provided that x+y+z is equal to the valence of M, which is selected from the group consisting of titanium or zirconium or hafnium.

15. The catalyst of Claim 14, wherein the metallocene compound is selected from the group consisting of bis-(cyclopentadienyl)zirconium dichloride and bis-(n-butylcyclopentadienyl)zirconium dichloride, 1,2-ethylene bis(indenyl)zirconium dichloride and 1,,1-ethylene bis(indenyl)zirconium dichloride.

16. The catalyst of Claim 15, wherein the metallocene compound is activated with a solution of methylalumoxane; wherein the silica has a pore volume in the range of 1.0 cc/g to 4.0 cc/g; wherein the solution has a volume which is equal to the total pore volume.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/11976

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 31/00, 31/26, 31/38

US CL :502/104, 107, 113, 115., 117

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/104, 107, 113, 115., 117

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---	US, A, 4,402,861 (HOFF) 06 September 1983, Whole document	1-14 -----
Y		15-16
Y	US, A, 4,707,530 (JOHNSON) 17 November 1987, Columns 3-8	1-16
Y	US, A, 4,910,272 (MARCHAND ET AL.) 20 March 1990, Columns 2-8	1-16
Y	US, A, 4,980,330 (MARCHAND ET AL.) 25 December 1990, Columns 2-7)	1-16
X	US, A, 5,032,562 (LO ET AL.) 16 July 1991, Whole document	1-16

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* "A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* "E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)	"A"	document member of the same patent family
* "O" document referring to an oral disclosure, use, exhibition or other means		
* "P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

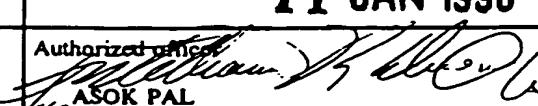
24 NOVEMBER 1995

Date of mailing of the international search report

11 JAN 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ASOK PAL

Telephone No. (703) 308-3809

